XI. On a new fulminating Mercury. By Edward Howard, Esq. F. R. S.

# Read March 13, 1800.

#### SECTION I.

The mercurial preparations which fulminate, when mixed with sulphur, and gradually exposed to a gentle heat, are well known to chemists: they were discovered, and have been fully described, by Mr. BAYEN.\*

MM. Brugnatelli and Van Mons have likewise produced fulminations by concussion, as well with nitrate of mercury and phosphorus, as with phosphorus and most other nitrates.† Cinnabar likewise is amongst the substances which, according to MM. Fourcroy and Vauquelin, detonate by concussion with oxymuriate of potash.‡

Mr. Ameilon had, according to Mr. Berthollet, observed, that the precipitate obtained from nitrate of mercury by oxalic acid, fuses with a hissing noise.§

- \* Opuscules Chimique de Bayen, Tom. I. p. 346, and note in p. 344.
- † Annales de Chimie, Tom. XXVII. p. 74 and 79.
- 1 Ibid. Tom. XXI. p. 238.
- § This fact has been misrepresented, in the introduction to a work intitled The chemical Principles of the metallic Arts, by W. RICHARDSON, surgeon, F. A. S. Sc. (page lvii.) The author, speaking of the acid of sorrel, says, "Klaproth of Berling precipitated a nitrous solution of mercury with acid of wood-sorrel, neutralized with

#### SECTION II.

But mercury, and most if not all its oxides, may, by treatment with nitric acid and alcohol, be converted into a whitish crystallized powder, possessing all the inflammable properties of gunpowder, as well as many peculiar to itself.

I was led to this discovery, by a late assertion, that hydrogen is the basis of the muriatic acid: it induced me to attempt to combine different substances with hydrogen and oxygen. With this view, I mixed such substances with alcohol and nitric acid, as I thought might (by predisposing affinity) favour, as well as attract, an acid combination, of the hydrogen of the one, and the oxygen of the other. The pure red oxide of mercury appeared not unfit for this purpose; it was therefore intermixed with alcohol, and upon both, nitric acid was affused. The acid did not act upon the alcohol so immediately as when these fluids are alone mixed together, but first gradually dissolved the oxide: however, after some minutes had elapsed, a smell of ether was perceptible, and a white dense smoke, much

<sup>&</sup>quot;vegetable alkali. The white precipitate, well washed and dried, produced a fulmi"nating noise, not inferior to that of fulminating gold. Acid of sugar, perfectly neu"tralized by vegetable alkali, produced the same precipitate, which, on exposure to
"heat, exhibited the same fulminating power." I must confess, I have not been able to
"produce any such fulmination. Mr. Richardson has moreover given this supposed
discovery to Mr. Klaproth; whereas, Mr. Berthollet, when quoting the fact to
which I suppose Mr. Richardson intended to allude, observes, "Qu'on avoit déjà
"donné le nom d'argent fulminant au précipité du nitrate d'argent par l'acide oxa"lique, dans lequel M. Klaproth avoit découvert la propriété de fuser avec vivacité
"lorsqu'on l'expose à la chaleur. M. Ameilon avoit aussi, depuis longtems, fait
"connoître que l'acide oxalique communiquoit cette propriété au mercure, quoique
"moins fortement qu'à l'argent; mais cet effet (he continues) est fort éloigné de
"celui qu'on désigne par la fulmination." Annales de Chimie, Tom. I. p. 57.

resembling that from the liquor fumans of Libavius, was emitted with ebullition. The mixture then threw down a dark-coloured precipitate, which by degrees became nearly white. This precipitate I separated by filtration; and, observing it to be crystallized in small acicular crystals, of a saline taste, and also finding a part of the mercury volatilized in the white fumes, I must acknowledge I was not altogether without hopes that muriatic acid had been formed, and united to the mercurial oxide. I therefore, for obvious reasons, poured sulphuric acid upon the dried crystalline mass, when a violent effervescence ensued, and, to my great astonishment, an explosion took place.

The singularity of this explosion induced me to repeat the process several times; and, finding that I always obtained the same kind of powder, I prepared a quantity of it, and was led to make the series of experiments which I shall have the honour to relate in this paper.

## SECTION III.

I first attempted to make the mercurial powder fulminate by concussion; and for that purpose laid about a grain of it upon a cold anvil, and struck it with a hammer, likewise cold: it detonated slightly, not being, as I suppose, struck with a flat blow; for, upon using 3 or 4 grains, a very stunning disagreeable noise was produced, and the faces both of the hammer and the anvil were much indented.

Half a grain or a grain, if quite dry, is as much as ought to be used on such an occasion.

The shock of an electrical battery, sent through 5 or 6 grains of the powder, produces a very similar effect: it seems indeed,

that a strong electrical shock, generally acts on fulminating substances like the blow of a hammer. Messrs. Fourcroy and VAUQUELIN found this to be the case with all their mixtures of oxymuriate of potash.\*

To ascertain at what temperature the mercurial powder explodes, 2 or 3 grains of it were floated on oil, in a capsule of leaf tin; the bulb of a Fahrenheit's thermometer was made just to touch the surface of the oil, which was then gradually heated till the powder exploded, as the mercury of the thermometer reached the 368th degree.

# SECTION IV.

Desirous of comparing the strength of the mercurial compound with that of gunpowder, I made the following experiment, in the presence of my friend Mr. Abernethy.

Finding that the powder could be fired by flint and steel, without a disagreeable noise, a common gunpowder proof, capable of containing eleven grains of fine gunpowder, was filled with it, and fired in the usual way: the report was sharp, but not loud. The person who held the instrument in his hand felt no recoil; but the explosion laid open the upper part of the barrel, nearly from the touch-hole to the muzzle, and struck off the hand of the register, the surface of which was evenly indented, to the depth of 0,1 of an inch, as if it had received the impression of a punch.

The instrument used in this experiment being familiarly known, it is therefore scarcely necessary to describe it; suffice it to say, that it was of brass, mounted with a spring register,

<sup>\*</sup> Annales de Chimie, Tom. XXI. p. 239.

the moveable hand of which closed up the muzzle, to receive and graduate the violence of the explosion. The barrel was half an inch in caliber, and nearly half an inch thick, except where a spring of the lock impaired half its thickness.

## SECTION V.

A gun belonging to Mr. Keir, an ingenious artist of Camdentown, was next charged with 17 grains of the mercurial powder, and a leaden bullet. A block of wood was placed at about eight yards from the muzzle, to receive the ball, and the gun was fired by a fuse. No recoil seemed to have taken place; as the barrel was not moved from its position, although it was in no ways confined. The report was feeble: the bullet, Mr. Keir conceived, from the impression made upon the wood, had been projected with about half the force it would have been by an ordinary charge, or 68 grains, of the best gunpowder. We therefore recharged the gun with 34 grains of the mercurial powder; and, as the great strength of the piece removed any apprehension of danger, Mr. Keir fired it from his shoulder, aiming at the same block of wood. The report was like the first in section IV. sharp, but not louder than might have been expected from a charge of gunpowder. Fortunately, Mr. Keir was not hurt, but the gun was burst in an extraordinary manner. The breech was what is called a patent one, of the best forged iron, consisting of a chamber 0,4 of an inch thick all round, and 0,4 of an inch in caliber; it was torn open and flawed in many directions, and the gold touch-hole driven out. The barrel, into which the breech was screwed, was 0,5 of an inch thick; it was split by a single crack three inches long, but this

did not appear to me to be the immediate effect of the explosion. I think the screw of the breech, being suddenly enlarged, acted as a wedge upon the barrel. The ball missed the block of wood, and struck against a wall, which had already been the receptacle of so many bullets, that we could not satisfy ourselves about the impression made by this last.

## SECTION VI.

As it was pretty plain that no gun could confine a quantity of the mercurial powder sufficient to project a bullet, with a greater force than an ordinary charge of gunpowder, I determined to try its comparative strength in another way.

I procured two blocks of wood, very nearly of the same size and strength, and bored them with the same instrument to the same depth. The one was charged with half an ounce of the best Dartford gunpowder, and the other with half an ounce of the mercurial powder; both were alike buried in sand, and fired by a train communicating with the powders by a small touch-hole. The block containing the gunpowder was simply split into three pieces: that charged with the mercurial powder was burst in every direction, and the parts immediately contiguous to the powder were absolutely pounded, yet the whole hung together, whereas the block split by the gunpowder had its parts fairly separated. The sand surrounding the gunpowder was undoubtedly most disturbed: in short, the mercurial powder appeared to have acted with the greatest energy, but only within certain limits.

#### SECTION VII.

The effects of the mercurial powder, in the last experiments, made me believe that it might be confined, during its explosion, in the centre of a hollow glass globe. Having therefore provided such a vessel, 7 inches in diameter, and nearly half an inch thick, mounted with brass caps, and a stop cock, (see Plate VIII.) I placed 10 grains of the mercurial powder on very thin paper, laid an iron wire 149th of an inch thick across the paper, through the midst of the powder, and, closing the paper, tied it fast at both extremities, with silk, to the wire. inclosed powder was now attached to the middle of the wire, each end of which was connected with the brass caps, the packet of powder became, by this disposition, fixed in the centre of the globe. Such a charge of an electrical battery was then sent along the wire, as a preliminary experiment\* had shewn me would, by making the wire red-hot, inflame the powder. The glass globe withstood the explosion, and of course retained whatever gases were generated: its interior was thinly coated with quicksilver in a very divided state. A bent glass tube was now screwed to the stop-cock of the brass cap, which being introduced under a glass jar standing in the mercurial bath, the stop-cock was opened. Three cubical inches of air rushed out, and a fourth was set at liberty when the apparatus was removed to the water-tub. The explosion being repeated, and the air all received over water, the quantity did not vary. To avoid an error from change of temperature, the glass globe was, both before and after the explosion, immersed in water of the same

temperature. It appears therefore, that the ten grains of powder, produced four cubical inches only of air.

To continue the comparison between the mercurial powder and gunpowder, 10 grains of the best Dartford gunpowder were in a similar manner set fire to in the glass globe: it remained entire. The whole of the powder did not explode, for some complete grains were to be observed adhering to the interior surface of the glass. Little need be said of the nature of the gases generated during the combustion of gunpowder: they must have been, carbonic acid gas, sulphureous acid gas, nitrogen gas, and (according to Lavoisier\*) perhaps hydrogen gas. As to the quantity of these gases, it is obvious that it could not be ascertained; because the two first were, at least in part, speedily absorbed by the alkali of the nitre, left pure after the decomposition of its nitric acid.

## SECTION VIII.

From the experiments related in the 4th and 5th sections, in which the gunpowder proof and the gun were burst, it might be inferred, that the astonishing force of the mercurial powder is to be attributed to the rapidity of its combustion; and, a train of several inches in length being consumed in a single flash, it is evident that its combustion must be rapid. From the experiments of the 6th and 7th sections, it is sufficiently plain that this force is restrained to a narrow limit; both because the block of wood charged with the mercurial powder was more shattered

<sup>\*</sup> See LAVOISIER, Traité elementaire, p. 527.

than that charged with the gunpowder, whilst the sand surrounding it was least disturbed; and likewise because the glass globe withstood the explosion of 10 grains of the powder fixed in its centre: a charge I have twice found sufficient to destroy old pistol barrels, which were not injured by being fired when full of the best gunpowder. It also appears, from the last experiment, that 10 grains of the powder, produced by ignition four cubical inches only of air; and it is not to be supposed that the generation, however rapid, of four cubical inches of air, will alone account for the described force; neither can it be accounted for by the formation of a little water, which, as will hereafter be shewn, happens at the same moment: the quantity formed from 10 grains must be so trifling, that I cannot ascribe much force to the expansion of its vapour. The sudden vaporization of a part of the mercury, seems to me a principal cause of this immense yet limited force; because its limitation may then be explained, as it is well known that mercury easily parts with caloric, and requires a temperature of 600 degrees of Fahrenheit, to be maintained in the vaporous state. That the mercury is really converted into vapour, by ignition of the powder, may be inferred from the thin coat of divided quicksilver, which, after the explosion in the glass globe, covered its interior surface; and likewise from the quicksilver with which a tallow candle, or a piece of gold, may be evenly coated, by being held at a small distance from the inflamed powder. These facts certainly render it more than probable, although they do not demonstrate, that the mercury is volatilized; because it is not unlikely that many mercurial particles are mechanically impelled against the surface of the glass, the gold, and the tallow.

As to the force of dilated mercury, Mr. BAUME' relates a remarkable instance of it, as follows.

"Un alchymiste se présenta à Mr. Geoffroy, et l'assura qu'il avoit trouvé le moyen de fixer le mercure par une opéra"tion fort simple. Il fit construire six boîtes rondes en fer fort épais, qui entroient les unes dans les autres; la derniere étoit assujettie par deux cercles de fer qui se croisoient en angles droits. On avoit mis quelques livres de mercure dans la capacité de la première: on mit cet appareil dans un fourneau assez rempli de charbon pour faire rougir à blanc les boîtes de fer; mais, lorsque la chaleur eut pénétré suffisamment le mercure, les boîtes creverent, avec une telle explosion qu'il se fit un bruit épouvantable: des morceaux de boîtes furent lancés avec tant de rapidité, qu'il y en eut qui passerent au travers de deux planchers; d'autres firent sur la muraille des effets semblables à ceux des éclats de bombes."\*

Had the alchemist proposed to fix water by the same apparatus, the nest of boxes must, I suppose, have likewise been ruptured; yet it does not follow that the explosion would have been so tremendous: indeed it is probable that it would not, for if (as Mr. Kirwan remarked to me) substances which have the greatest specific gravity, have likewise the greatest attraction of cohesion, the supposition that the vapour of mercury exceeds in expansive force the vapour of water, would agree with a position of Sir Isaac Newton, that those particles recede from one another with the greatest force, and are most difficultly brought together, which upon contact cohere most strongly.

<sup>\*</sup> Chymie expérimentale et raisonnée, Tom. II. p. 393. Paris, 8°, 1773.

<sup>†</sup> Newton's Optics, p. 372, 4th Ed. Lond. 1730.

## SECTION IX.

Before I attempt to investigate the constituent principles of this powder, it will be proper to describe the process and manipulations which, from frequent trials, seem to me best calculated to produce it.

100 grains, or a greater proportional quantity, of quicksilver (not exceeding 500 grains\*) are to be dissolved, with heat, in a measured ounce and a half of nitric acid. + This solution being poured cold upon two measured ounces of alcohol, previously introduced into any convenient glass vessel, a moderate heat is to be applied until an effervescence is excited. A white fume then begins to undulate on the surface of the liquor; and the powder will be gradually precipitated, upon the cessation of action and re-action. The precipitate is to be immediately collected on a filter, well washed with distilled water, and carefully dried in a heat not much exceeding that of a water bath. The immediate edulcoration of the powder is material, because it is liable to the re-action of the nitric acid; and, whilst any of that acid adheres to it, it is very subject to the influence of light. Let it also be cautiously remembered, that the mercurial solution is to be poured upon the alcohol.

I have recommended quicksilver to be used in preference to an oxide, because it seems to answer equally, and is less expen-

<sup>\*</sup> The reason of this limitation is not on account of any danger attending the process; but because the quantities of nitric acid and alcohol required for more than 500 grains, would excite a degree of heat detrimental to the preparation.

<sup>+</sup> Of the specific gravity of about 1,3.

<sup>†</sup> Of the specific gravity of about ,849.

sive; otherwise, not only the pure red oxide, but the red nitrous oxide, and turpeth, may be substituted; neither does it seem essential to attend to the precise specific gravity of the acid, or the alcohol. The rectified spirit of wine and the nitrous acid of commerce, never failed, with me, to produce a fulminating mercury. It is indeed true, that the powder prepared without attention, is produced in different quantities, varies in colour, and probably in strength. From analogy, I am disposed to think the whitest is the strongest; for it is well known, that black precipitates of mercury approach the nearest to the metallic The variation in quantity is remarkable; the smallest quantity I ever obtained from 100 grains of quicksilver being 120 grains, and the largest 132 grains. Much depends on very minute circumstances. The greatest product seems to be obtained, when a vessel is used which condenses and causes most ether to return into the mother liquor; besides which, care is to be had in applying the requisite heat, that a speedy, and not a violent action be effected. 100 grains of an oxide are not so productive as 100 grains of quicksilver.

As to the colour, it seems to incline to black, when the action of the acid on the alcohol is most violent, and *vice versá*.

## SECTION X.

I need not observe, that the gases which were generated during the combustion of the powder in the glass globe, were necessarily mixed with atmospheric air; the facility wi h which the electric fluid passes through a vacuum, made such a mixture unavoidable.

The cubical inch of gas received over water was not readily

absorbed by it: and, as it soon extinguished a taper, without becoming red, or being itself inflamed, barytes water was let up to the three cubical inches received over mercury, when a carbonate of barytes was immediately precipitated.

The residue of several explosions, after the carbonic acid had been separated, was found, by the test of nitrous gas, to contain nitrogen or azotic gas; which does not proceed from any decomposition of atmospheric air, because the powder may be made to explode under the exhausted receiver of an air-pump. It is therefore manifest, that the gases generated during the combustion of the fulminating mercury, consist of carbonic acid and nitrogen gases.

## SECTION XI.

The principal re-agents which decompose the mercurial powder, are the nitric, the sulphuric, and the muriatic acids. The nitric changes the whole into nitrous gas, carbonic acid gas, acetous acid, and nitrate of mercury. I resolved it into these different principles, by distilling it pneumatically with nitric acid: this acid, upon the application of heat, soon dissolved the powder, and extricated a quantity of gas, which was found, by well known tests, to be nitrous gas mixed with carbonic acid gas. The distillation was carried on until gas no longer came over. The liquor of the retort was then mixed with the liquor collected in the receiver, and the whole saturated with potash; which precipitated the mercury in a yellow-ish-brown powder, nearly as it would have done from a solution of nitrate of mercury. This precipitate was separated by a filter,

and the filtrated liquor evaporated to a dry salt, which was washed with alcohol. A portion of the salt being refused by this menstruum, it was separated by filtration, and recognized, by all its properties, to be nitrate of potash. The alcoholic liquor was likewise evaporated to a dry salt, which, upon the affusion of a little concentrate sulphuric acid, emitted acetous acid, contaminated with a feeble smell of nitrous acid, owing to the solubility of a small portion of the nitre in the alcohol.

#### SECTION XII.

The sulphuric acid acts upon the powder in a remarkable manner, as already has been noticed. A very concentrate acid produces an explosion nearly at the instant of contact, on account, I presume, of the sudden and copious disengagement of caloric from a portion of the powder which is decomposed by the acid. An acid somewhat less concentrate likewise extricates a considerable quantity of caloric, with a good deal of gas; but, as it effects a complete decomposition, it causes no explosion. An acid diluted with an equal quantity of water, by the aid of a little heat, separates the gas so much less rapidly, that it may with safety be collected in a pneumatic apparatus. But, whatever be the density of the acid, (provided no explosion be produced,) there remains in the sulphuric liquor, after the separation of the gas, a white uninflammable and uncrystallized powder, mixed with some minute globules of quicksilver.

To estimate the quantity, and observe the nature, of this uninflammable substance, I treated 100 grains of the fulminating mercury with sulphuric acid a little diluted. The gas being separated, I decanted off the liquor as it became clear, and freed the insoluble powder from acid, by edulcoration with distilled

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water; after which, I dried it, and found it weighed only 84 grains; consequently had lost 16 grains of its original weight. Suspecting, from the operation of the nitric acid in the former experiment, that these 84 grains (with the exception of the quicksilver globules) were oxalate of mercury, I digested them in nitrate of lime, and found my suspicion just. The mercury of the oxalate united to the nitric acid, and the oxalic acid to the lime. A new insoluble compound was formed; it weighed; when washed and dry, 48,5 grains. Carbonate of potash separated the lime, and formed oxalate of potash, capable of precipitating lime-water, and muriate of lime; although it had been depurated from excess of alkali, and from carbonic acid, by a previous addition of acetous acid. That the mercury of the oxalate in the 84 grains, had united to the nitric acid of the nitrate of lime, was proved by dropping muriatic acid into the liquor from which the substance demonstrated to be oxalate of lime had been separated; for a copious precipitation of calomel instantly ensued.

The sulphuric liquor, decanted from the oxalate of mercury, was now added to that with which it was edulcorated, and the whole saturated with carbonate of potash. As effervescence ceased, a cloudiness and precipitation followed; and the precipitate, being collected, washed, and dried, weighed 3,4 grains: it appeared to be a carbonate of mercury. Upon evaporating a portion of the saturated sulphuric liquor, I found nothing but sulphate of potash; nor had it any metallic taste. There then remains, without allowing for the weight of the carbonic acid united to the 3,4 grains, a deficit from the 100 grains of mercurial powder, of 12,6 grains, which I ascribe to the gas separated by the action of the sulphuric acid. To ascertain the quantity, and examine the nature, of the gas so separated, I introduced into a

very small tubulated retort, 50 grains of the mercurial powder, and poured upon it 3 drams, by measure, of sulphuric acid, diluted with an equal quantity of water, and extricated the gas with the assistance of a gentle heat. I first received it over quicksilver, the surface of which, during the operation, partially covered itself with a little black powder.\*

The gas, by different trials, amounted from 28 to 31 cubical inches; it at first appeared to be nothing but carbonic acid, as it precipitated barytes water, and extinguished a taper, without being itself inflamed, or becoming red. But, upon letting up to it liquid caustic ammoniac, there was a residue of from 5 to 7 inches of a peculiar inflammable gas, which burnt with a greenish blue flame. When I made use of the water-tub, I obtained, from the same materials, from 25 to 27 inches only of gas, although the average quantity of the peculiar inflammable gas was likewise from 5 to 7 inches; therefore, the difference of the aggregate product, over the two fluids, must have arisen from the absorption, by the water, of a part of the carbonic acid in its nascent state. The variation of the quantity of the inflammable gas, when powder from the same parcel is used, seems to depend upon the acid being a little more or less dilute.

With respect to the nature of the peculiar inflammable gas, it is plain to me, from the reasons I shall immediately adduce, that it is no other than the gas (in a pure state) into which the nitrous etherized gas can be resolved, by treatment with dilute sulphuric acid.

The Dutch chemists have shewn, that the nitrous etherized gas can be resolved into nitrous gas, by exposure to concentrate

<sup>\*</sup> I cannot account for this appearance.

<sup>†</sup> Journal de Physique, p. 250, October, 1794.

sulphuric acid, and that, by using a dilute instead of a concentrate acid, a gas is obtained which enlarges the flame of a burning taper, so much like the gaseous oxide of azote, that they mistook it for that substance, until they discovered that it was permanent over water, refused to detonate with hydrogen, and that the fallacious appearance was owing to a mixture of nitrous gas with an inflammable gas.

The inflammable gas separated from the powder answers to the description of the gas which at first deceived the Dutch chemists; 1st, in being permanent over water; 2dly, refusing to detonate with hydrogen; and, 3dly, having the appearance of the gaseous oxide of azote, when mixed with nitrous gas.

The gas separable by the same acid, from nitrous etherized gas, and from the mercurial powder, have therefore the same properties. Every chemist would thence conclude, that the nitrous etherized gas is a constituent part of the powder, had the inflammable and nitrous gas, instead of the inflammable and carbonic acid gas, been the mixed product extricated from it by dilute sulphuric acid.

It however appears to me, that nitrous gas was really produced by the action of the dilute sulphuric acid; and that, when produced, it united to an excess of oxygen present in the oxalate of mercury.

To explain how this change might happen, I must premise, that my experiments have shewn me, that oxalate of mercury can exist in two, if not in three states.

1st, By the discovery of Mr. Ameilon already quoted, the precipitate obtained by oxalic acid, from nitrate of mercury, fuses with a hissing noise. This precipitate is an oxalate of mercury, seemingly with excess of oxygen. Mercury dissolved in sul-

phuric acid and precipitated by oxalic acid, and also the pure red oxide of mercury digested with oxalic acid, give oxalates in the same state.

adly. Acetate of mercury precipitated by oxalic acid, although a true oxalate is formed, has no kind of inflammability. I consider it as an oxalate with less oxygen than those abovementioned.

gdly. A solution of nitrate of mercury boiled with dulcified spirit of nitre, gives an oxalate more inflammable than any other: perhaps it contains most oxygen.

The oxalate of mercury remaining from the powder in the sulphuric liquor, is not only always in the same state as that precipitated from acetate of mercury, entirely devoid of inflammability, but contains globules of quicksilver; consequently, it must have parted with even more than its excess of oxygen; and, if nitrous gas was present, it would of course seize at least a portion of that oxygen. It is true, that globules of quicksilver may seem incompatible with nitrous acid; but the quantity of the one may not correspond with that of the other, or the dilution of the acid may destroy its action.

As to the presence of the carbonic acid, it must have arisen either from a complete\* decomposition of a part of the oxalate; or, admitting the nitrous etherized gas to be a constituent principle of the powder, from a portion of the oxygen, not taken up by the nitrous gas, being united with the carbon of the etherized gas.

## SECTION XIII.

The muriatic acid digested with the mercurial powder, dis-

<sup>\*</sup> Inflammable oxalate of mercury, made to fuse in a retort connected with the quicksilver tub, gives out carbonic acid gas.

222

solves a portion of it, without extricating any notable quantity of gas. The dissolution evaporated to a dry salt, tastes like corrosive sublimate; and the portion which the acid does not take up, is left in the state of an uninflammable oxalate.

## SECTION XIV.

These effects all tend to establish the existence of the nitrous etherized gas, as a constituent part of the powder; and likewise corroborate the explanation I have ventured to give, of the action of the sulphuric acid. Moreover, a measured ounce and a half of nitrous acid, holding 100 grains of mercury in solution, and 2 measured ounces of alcohol, yield 90 cubical inches only of gas: whereas, without the intervention of mercury, they yield 210 inches. Upon the whole, I trust it will be thought reasonable to conclude, that the mercurial powder is composed of the nitrous etherized gas, and of oxalate of mercury with excess of oxygen.

1st. Because the nitric acid converts the mercurial powder entirely into nitrous gas, carbonic acid gas, acetous acid, and nitrate of mercury.

2dly. Because the dilute sulphuric acid resolves it into an uninflammable oxalate of mercury, and separates from it a gas resembling that into which the same acid resolves the nitrous etherized gas.

3dly. Because an uninflammable oxalate is likewise left, after the muriatic acid has converted a part of it into sublimate.

4thly. Because it cannot be formed by boiling nitrate of mercury in dulcified spirit of nitre; although a very inflammable oxalate is by this means produced.

5thly. Because the difference of the product of gas, from the

same measures of alcohol and nitrous acid, with and without mercury in solution, is not trifling; and,

6thly. Because nitrogen gas was generated during its combustion in the glass globe.

Should my conclusions be thought warranted by the reasons I have adduced, the theory of the combustion of the mercurial powder will be obvious to every chemist. The hydrogen of the oxalic acid, and of the etherized gas, is first united to the oxygen of the oxalate, forming water;\* the carbon is saturated with oxygen, forming carbonic acid gas; and a part, if not the whole of the nitrogen of the etherized gas, is separated in the state of nitrogen gas; both which last gases, it may be recollected, were after the explosion present in the glass globe. The mercury is revived, and, I presume, thrown into vapour; as may well be imagined, from the immense quantity of caloric extricated, by adding concentrate sulphuric acid to the mercurial powder.

I will not venture to state with accuracy, in what proportions its constituent principles are combined. The affinities I have brought into play are complicated, and the constitution of the substances I have to deal with not fully known. But, to make round numbers, I will resume the statement, that 100 grains of the mercurial powder lost 16 grains of its original weight, by treatment with dilute sulphuric acid: 84 grains of mercurial oxalate, mixed with a few minute globules of quicksilver, remained undissolved in the acid. The sulphuric liquor was saturated with carbonate of potash, and yielded 3,4 grains of carbonate of mercury. If 1,4 grain should be thought a proper

<sup>•</sup> Drops of water were observed on the internal surface of the globe, the day afterseveral explosions had been produced in its centre.

allowance for the weight of carbonic acid in the 3,4 grains, I will make that deduction, and add the remaining 2 grains to the 84 grains of mercurial oxalate and quicksilver; I shall then have,

of oxalate and mercury - - - 86 grains and a deficit, to be ascribed to the nitrous etherized gas and excess of oxygen - - 14

It may perhaps be proper to proceed still further, and recur to the 48,5 grains, separated by nitrate of lime from the 84 grains of mercurial oxalate and globules of quicksilver, in the 11th section. These 48,5 grains were proved to be chiefly oxalate of lime; but they likewise contained a minute inseparable quantity of mercury, almost in the state of quicksilver, formerly part of the 84 grains from which they were separated. Had the 48,5 grains been pure calcareous oxalate, the quantity of pure oxalic acid in them would, according to Bergmann,\* be 23,28 grains. Hence, by omitting the 2 grains of mercury in the 3,4 grains of carbonate, 100 grains of the mercurial powder might have been said to contain, of pure oxalic acid 23,28 grains; of mercury 62,72 grains; and of nitrous etherized gas and excess of oxygen 14 grains. But, as the 48,5 grains were not pure oxalate, inasmuch as they contained the mercury they received from the 84 grains, from which they were generated by the nitrate of lime, some allowance must be made for the mercury successively intermixed with the 84 grains and the 48,5 grains.

In order to make corresponding numbers, and allow for unavoidable errors, I shall estimate the quantity of that mercury to have amounted to 2 grains, which I must of course deduct

<sup>\*</sup> Bergmann, de Acido Sacchari. Opuscula. Tom. I. § 6. p. 248. Leipzig, 1788.

from the 23,28 grains of oxalic acid. I shall then have the following statement:

That 100 grains of the fulminating mercury ought to contain, of pure oxalic acid 21,28 grains, of mercury formerly united to the oxalic acid 60,72 of mercury dissolved in the sulphuric liquor and of mercury left in the sulphuric liquor after the separation of the gases 2 Total of mercury 64,72 Of nitrous etherized gas and excess of oxygen 100.

Since 100 grains of the powder seem to contain 64,72 grains of mercury, it will be immediately inquired, what becomes of 100 grains of quicksilver, when treated as directed, in the description of the process for preparing the fulminating mercury.

It has been stated (in section 9.) that 100 grains of quicksilver produce, under different circumstances, from 120 to 132 grains of mercurial powder; and, if 100 grains of this powder contain 64,72 grains, 120 grains, or 132 grains must, by parity of reasoning, contain 78,06 grains, or 85,47 grains; therefore, 13,34 grains, or 20,75 grains, more of the 100 grains are immediately accounted for; because 64,72 grains + 13,34 grains = 78,06, and 64,72 grains +20,75 grains =85,47 grains. The remaining deficiency of 21,94 grains, or 14,53 grains, which, with the 78,06 grains, or 85,47 grains, would complete the original 100, of quicksilver, remains partly in the liquor from which the powder is separated, and is partly volatilized in the white dense fumes, which in the beginning of this paper I compared to the liquor fumans of Libavius. The mercury cannot, in either MDCCC.

instance, be obtained in a form immediately indicative of its quantity; and a series of experiments to ascertain the quantities in which many different substances can combine with mercury, is not my present object. After observing, that the mercury left in the residuary liquor can be precipitated in a very subtle dark powder, by carbonate of potash, I shall content myself with examining the nature of the white fumes.

# SECTION XV.

It is clear that these white fumes contain mercury: they may be wholly condensed in a range of Woulfe's apparatus, charged with a solution of muriate of ammoniac. When the operation is over, a white powder is seen floating with ether on the saline liquor, which, if the bottles are agitated, is entirely dissolved. After the mixture has been boiled, or for some time exposed to the atmosphere, it yields to caustic ammoniac a precipitate, in all respects similar to that which is separated by caustic ammoniac from corrosive sublimate.

I would infer from these facts, that the white dense fumes consist of mercury, or perhaps oxide of mercury, united to the nitrous etherized gas; and that, when the muriate of ammoniac containing them is exposed to the atmosphere, or is boiled, the gas separates from the mercury; and the excess of nitrous acid, which always comes over with nitrous ether, decomposes the ammoniacal muriate, and forms corrosive mercurial muriate or sublimate. This theory is corroborated, by comparing the quantity of gas estimated to be contained in the fulminating mercury, with the quantities of gas yielded from alcohol and nitrous acid, with and without mercury in solution; not to mention that more ether, as well as more gas, is produced without the inter-

vention of mercury; and that, according to the Dutch chemists, the product of ether, is always in the inverse ratio to the product of nitrous etherized gas. Should a further proof be thought necessary, of the existence of the nitrous etherized gas in the fulminating mercury, as well as in the white dense fumes, it may be added, that if a mixture of alcohol and nitrous acid holding mercury in solution, be so dilute, and exposed to a temperature so low, that neither ether nor nitrous etherized gas are produced, the fulminating mercury, or the white fumes, will never be generated: for, under such circumstances, the mercury is precipitated chiefly in the state of an inflammable oxalate. Further, when we consider the different substances formed by an union of nitrous acid and alcohol, we are so far acquainted with all, except the ether and the nitrous etherized gas, as to create a presumption, that no others are capable of volatilizing mercury, at the very low temperature in which the white fumes exist, since during some minutes they are permanent over water of 40° Fahrenheit.

## SECTION XVI.

Hitherto, as much only has been said of the gas which is separated from the mercurial powder by dilute sulphuric acid, as was necessary to identify it with that into which the same acid can resolve the nitrous etherized gas; I have further to speak of its peculiarity.\*

<sup>\*</sup> It must be first noticed, that it is never pure when obtained from the nitrous etherized gas; nor am I aware how it is to be purified, unless the nitrous gas could be taken from it, without being converted into nitrous acid; for, by that acid, it would probably be itself converted into nitrous gas.

The characteristic properties of the inflammable gas, seem to me to be the following:

1st. It does not diminish in volume, either with oxygen or nitrous gas.

2dly. It will not explode with oxygen by the electric shock, in a close vessel.

3dly. It burns like hydrocarbonate, but with a bluish green flame. And,

4thly. It is permanent over water. (Section 12.)

It is of course either not formed, or is convertible into nitrous gas, by the concentrate nitric and muriatic acids; because, by those acids, no inflammable gas was extricated from the powder.

Should this inflammable gas prove not to be a hydrocarbonate, I shall be disposed to conclude, that it has nitrogen for its basis; indeed, I am at this moment inclined to that opinion, because I find that Dr. PRIESTLEY, during his experiments on his dephlogisticated nitrous air, once produced a gas which seems to have resembled this inflammable gas, both in the mode of burning, and in the colour of the flame.

After the termination of the common solution of iron in spirit of nitre, he used heat, and got, says he,\* "such a kind "of air as I had brought nitrous air to be, by exposing it to "iron, or liver of sulphur; for, on the first trial, a candle burned in it with a much enlarged flame. At another time, the application of a candle to air produced in this manner, was attended with a real though not a loud explosion; and, immediately after this, a greenish coloured flame descended from the top to the bottom of the vessel in which the air was

<sup>\*</sup> PRIESTLEY on Air, Vol. II. p. 58. Birmingham. 1790.

"contained. In the next produce of air, from the same process, "the flame descended blue and very rapid, from the top to the bottom of the vessel."

These greenish and blue coloured flames, descending from the top to the bottom of the vessel, are precisely descriptive of the inflammable gas separated from the powder. If it can be produced with certainty by the repetition of Dr. PRIESTLEY's experiments, or should it by any means be got pure from the nitrous etherized gas, my curiosity will excite me to make it the object of future research; otherwise, I must confess, I shall feel more disposed to prosecute other chemical subjects: for, having reason to think that the density of the acid made a variation in the product of this gas, and having never found that any acid, however dense, produced an immediate explosion, I once poured 6 drams of concentrate acid upon 50 grains of the powder. An explosion, nearly at the instant of contact, was effected: I was wounded severely, and most of my apparatus destroyed. A quantity moreover of the gas I had previously prepared, was lost by the inadvertency of a person who went into my laboratory, whilst I was confined by the consequences of this discouraging accident. But, should any one be desirous of giving the gas a further examination, I again repeat, that as far as I am enabled to judge, it may with safety be prepared, by pouring g drams of sulphuric acid diluted with the same quantity of water, upon 50 grains of the powder, and then applying the flame of a candle until gas begins to be extricated. The only attempt I have made to decompose it, was by exposing it to copper and ammoniac; which, during several weeks, did not effect the least alteration.

## SECTION XVII.

I will now conclude, by observing, that the fulminating mercury seems to be characterised by the following properties.

It takes fire at the temperature of 368 FAHRENHEIT; explodes by friction,\* by flint and steel, and by being thrown into concentrate sulphuric acid. It is equally inflammable under the exhausted receiver of an air-pump, as surrounded by atmospheric air; and it detonates loudly, both by the blow of a hammer, and by a strong electrical shock.

Notwithstanding the composition of fulminating silver, and of fulminating gold, differ essentially from that of fulminating mercury, all three have some similar qualities. In tremendous effects, silver undoubtedly stands first, and gold perhaps the last. The effects of the mercurial powder and of gunpowder, admit of little comparison. The one exerts, within certain limits, an almost inconceivable force: its agents seem to be gas and caloric, very suddenly set at liberty, and both mercury and water thrown into vapour. The other displays a more extended but inferior power: gas and caloric are, comparatively speaking, liberated by degrees; and water, according to Count Rumford, is thrown into vapour.

Hence it seems, that the fulminating mercury, from the limitation of its sphere of action; can seldom if ever be applied to mining; and, from the immensity of its initial force, cannot be

- \* Consequently it should not be inclosed in a bottle with a glass stopper.
- + See Philosophical Transactions, for the year 1797, p. 222.

The hard black substance mentioned by the Count, as remaining after the combustion of gunpowder, must, I believe, have been an alkaline sulphuret, mixed chiefly with sulphite and carbonate of potash. The conjecture that it is white when first formed, is certainly just, as my experiment with the glass globe evinced.

used in fire-arms, unless in cases where it becomes an object to destroy them; perhaps, where it is the practice to spike cannon, it may be of service, because, I apprehend, it may be used in such a manner as to burst cannon, without dispersing any splinters.

The inflammation of fulminating mercury by concussion, offers nothing more novel or remarkable, than the inflammation, by concussion, of many other substances. The theory of such inflammations has been long since exposed by the celebrated Mr. Berthollet, and confirmed by Messieurs Fourcroy and VAUQUELIN: yet, I must confess, I am at a loss to understand, why a small quantity of mercurial powder made to detonate by the hammer, or the electric shock, should produce a report so much louder than when it is inflamed by a match, or by flint and steel. It might at first be imagined, that the loudness of the report could be accounted for, by supposing the instant of the inflammation, and that of the powder's confinement between the hammer and anvil, to be precisely the same; but, when the electrical shock is sent through or over a few grains of the powder, merely laid on ivory, and a loud report is the consequence, I can form no idea of what causes such a report.

The operation by which the powder is prepared, is perhaps one of the most beautiful and surprising in chemistry; and it is not a little interesting to consider the affinities which are brought into play. The superabundant nitrous acid of the mercurial solution, must first act on the alcohol, and generate ether, nitrous etherized gas, and oxalic acid. The mercury unites to the two last in their nascent state, and relinquishes fresh nitrous acid, to act upon any unaltered alcohol. The oxalic acid, although a predisposing affinity seems exerted in favour of its quantity, is evidently not formed fast enough to retain all the

mercury; otherwise, no white fumes, during a considerable period of the operation, but fulminating mercury alone, would be produced.

Should any doubt still be entertained of the existence of the affinities which have been called predisposing or conspiring, a proof that such affinities really exist, will I think be afforded, by comparing the quantity of oxalic acid which can be generated from given measures of nitrous acid and alcohol, with the intervention of mercury, and the intervention of other metals. For instance, when two measured ounces of alcohol are treated with a solution of 100 grains of nickel in a measured ounce and a half of nitrous acid, little or no precipitate is produced; yet, by the addition of oxalic acid to the residuary liquor, a quantity of oxalate of nickel, after some repose, is deposited. Copper affords another illustration: 100 grains of copper, dissolved in a measured ounce and a half of nitrous acid, and treated with alcohol, yielded me about 18 grains only of oxalate; although cupreous oxalate was plentifully generated, by dropping oxalic acid into the residuary liquor. About 21 grains of pure oxalic acid seem to be produced, from the same materials, when 100 grains of mercury are interposed. (See section 14.) Besides, according to the Dutch paper, more than once referred to, acetous acid is the principal residue after the preparation of nitrous ether. How can we explain the formation of a greater quantity of oxalic acid, from the same materials, with the intervention of 100 grains of mercury, than with the intervention of 100 grains of copper, otherwise than by the notion of conspiring affinities, so analogous to what we see in other phænomena of nature?

I have attempted, without success, to communicate fulminating properties, by means of alcohol, to gold, platina, antimony, tin, copper, iron, lead, zinc, nickel, bismuth, cobalt,

arsenic, and manganese; but I have not yet sufficiently varied my experiments, to enable me to speak with absolute certainty. Silver, when 20 grains of it were treated with nearly the same proportions of nitrous acid and alcohol as 100 grains of mercury, yielded, at the end of the operation, about 3 grains of a gray precipitate, which fulminated with extreme violence. CRUICKSHANK had the goodness to repeat the experiment: he dissolved 40 grains of silver in 2 ounces of the strongest nitrous acid diluted with an equal quantity of water, and obtained (by means of 2 ounces of alcohol) 60 grains of a very white powder, which fulminated like the gray precipitate above described. It probably combines with the same principles as the mercury, and of course differs from Mr. Berthollet's fulminating silver, alluded to in page 230. I observe, that a white precipitate is always produced in the first instance, and that it may be preserved, by adding water, as soon as it is formed; otherwise, when the mother liquor is abundant, it often becomes gray, and is re-dissolved.

P. S. Since the preceding pages were written, I have been permitted, by the Right Honourable Lord Howe, Lieutenant General of the Ordnance, to make the following trials of the mercurial powder, at Woolwich, in conjunction with Colonel Blomefield, and Mr. Cruickshank.\*

Experiment 1. From the manner in which the screw of the gunbreech, mentioned in Section v. had acted on the barrel, it was imagined, that by bursting an iron case, exactly fitted to the bore of a cannon, its sudden enlargement might make many flaws, and split the piece, without dispersing any splinters. In

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<sup>\*</sup> It is with pleasure I take this opportunity of acknowledging the civil attention I received from the different officers.

conformity to this opinion, a cast iron case was constructed, with a cylindrical chamber, of equal length and diameter, calculated to hold 31th ounces troy of the mercurial powder. The case, being firmly screwed together, was charged through its vent-hole, and introduced into a twelve-pounder carronade, the bore of which it exactly fitted. The powder was then enflamed, with proper precautions. The gun remained entire, but the case divided: the portion forming the upper surface of the chamber, was expelled in one mass; that adjoining the breech, which constituted the rest of the chamber, was cracked in every direction, and in part crumbled; yet it was so wedged into some indentations which the explosion had made in the sides of the piece, that the fragments were not removed without great labour.

Exp. 2. Another cast iron case was prepared, of the same size as the former, with a chamber also cylindrical, but wrought in a transverse direction, and of a greater length than diameter; the thickness of metal at each extremity not being more than a quarter of an inch. This case was filled with nearly 5 ounces troy of the mercurial powder, and placed in the same carronade. Three twelve-pound shot were next introduced, and brought into close contact with the upper surface of the case, as well as with each other. The gun a second time withstood the explosion: the case was divided across the middle of the chamber, into two equal parts; that adjoining the breech was, as in the former experiment, much flawed, and left immoveable; that nearest to the muzzle was also much flawed, but driven out with the shot. All the three shot were broken; the two lower being divided into several pieces, and the upper one cracked through the centre.

The report was so feeble, in both experiments, that an inattentive person, I am confident, would not have heard it at the distance of two hundred yards.

Exp. 3. It was found so difficult to extract the fragments of the case remaining in the carronade, after the last experiment, that a channel was drilled through them, to the vent-hole of the piece. It was then charged with 6 ounces troy of the mercurial powder, made up as a cartridge, which did not occupy above one half of the diameter of the bore. A wad was placed over the powder, dry sand superadded, to fill all vacuities, and the gun filled to the muzzle with two twelve-pound shot. A block of wood was set at a small distance, to receive the impression of the shot, and the powder was inflamed as usual. The carronade still resisted. One of the shot was split into two pieces; and the block of wood was driven to a considerable distance, but not penetrated by the shot above the depth of one inch. The report was somewhat louder than the former ones. In all three instances, a considerable recoil evidently took place. I presume, therefore, that in the first experiment related in the fifth Section, there must have been a recoil, though too trifling to be observed; and, in the instances where the gun and the proof were burst, it was not so much to be expected.

Exp. 4. Finding that the carronade, from the great comparative size of its bore to that of its length, required a larger quantity of mercurial powder to burst it than we were provided with, we charged a half-pounder swivel with an ounce and an half avoirdupois of the mercurial powder, (the service charge of gunpowder being 3 ounces,) and a half-pound shot between two wads. The piece was destroyed from the trunnions to the breech, and its fragments thrown thirty or forty yards. The ball penetrated five inches into a block of wood, standing at about a yard from the muzzle of the gun; the part of the swivel not broken, was scarce, if at all, moved from its original position.

Exp. 5. One ounce avoirdupois of the mercurial powder,

enclosed in paper, was placed in the centre of a shell 4,4 inches in diameter, and the vacant space filled with dry sand.

The shell burst by the explosion of the powder, and the fragments were thrown to a considerable distance. The charge of gunpowder employed to burst shells of this diameter, is 5 ounces avoirdupois.

Exp. 6. A sea grenade, 3,5 inches diameter, charged like the shell in the last experiment, was burst into numerous fragments, by  $\frac{1}{4}$  of an ounce avoirdupois of the mercurial powder. The fragments were projected with but little force, and only to the distance of eight or ten yards. The charge of gunpowder required for grenades of this size, is 3 ounces.

*Exp.* 7. A sea grenade, of the same diameter as the last mentioned, and charged in the like manner, with  $\frac{1}{8}$  of an ounce avoirdupois, or  $57\frac{1}{2}$  grains, of the mercurial powder, was split into two equal pieces, which were not thrown ten inches asunder.

The report in the four last experiments was very sharp, but not loud in proportion.

It seems, from the manner in which the swivel was burst, in the fourth experiment, that a smaller charge would have been sufficient for the purpose. We may therefore infer, both from this instance and from the second experiment made with the gun, in Section v, that any piece of ordnance might be destroyed, by employing a quantity of the mercurial powder equal in weight to one half of the service charge of gunpowder; and, from the seventh and last experiment, we may also conclude, that it would be possible so to proportion the charge of mercurial powder to the size of different cannons, as to burst them without dispersing any splinters. But the great danger attending the use of fulminating mercury, on account of the facility with which it explodes, will probably prevent its being employed for that purpose.

In addition to the other singular properties of the fulminating mercury, it may be observed, that two ounces inflamed in the open air, seem to produce a report much louder than when the same quantity is exploded in a gun capable of resisting its action. Mr. Cruickshank, who made some of the powder, by my process, remarked that it would not inflame gunpowder. In consequence of which, we spread a mixture of coarse and fine grained gunpowder upon a parcel of the mercurial powder; and, after the inflammation of the latter, we collected most, if not all, of the grains of gunpowder. Can this extraordinary fact be explained by the rapidity of the combustion of fulminating mercury? or is it to be supposed, (as gunpowder will not explode at the temperature at which mercury is thrown into vapour,) that sufficient caloric is not extricated during this combustion?

From the late opportunity I have had of conversing with Mr. Cruickshank, I find that he has made many accurate experiments on gunpowder; and he has permitted me to state, "that the matter which remains after the explosion of gun-"powder, consists of potash united with a small proportion of carbonic acid, sulphate of potash, a very small quantity of sulphuret of potash, and unconsumed charcoal. That 100 grains of good gunpowder yield about 53 grains of this residuum, of which three are charcoal. That it is extremely deliquescent, and, when exposed to the air, soon absorbs moisture sufficient to dissolve a part of the alkali; in consequence of which, the charcoal becomes exposed, and the whole assumes a black or very dark colour." Mr. Cruickshank likewise informs me, that after the combustion of good gunpowder under mercury, no water is ever perceptible.

REFERENCES TO THE FIGURES OF THE GLASS GLOBE, &c.MENTIONED IN SECTION VII.

# (See Plate VIII.)

A, a ball or globe of glass, nearly half an inch thick, and seven inches in diameter. It has two necks, on which are cemented the brass caps B, C, each being perforated with a female screw, to receive the male ones D, E: through the former a small hole is drilled; the latter is furnished with a perforated stud or shank G. By means of a leather collar H, the neck C can be air-tightly closed. When a portion of the powder is to be exploded, it must be placed on a piece of paper, and a small wire laid across the paper, through the midst of the powder: the paper being then closed, is to be tied at each end to the wire, with a silken thread, as shewn at I. One end of this wire is to be fastened to the end of the shank G, and the screw D inserted to half its length into the brass cap B; the other end of the wire, a, by means of the needle K, is to be drawn through the hole F. The screw E being now fixed in its place, and the wire drawn tight, it is to be secured, by pushing the irregular wooden plug L into the aperture of the screw D, taking care to leave a passage for air. The stop-cock M, the section of which is shewn at N, is now to be screwed on to the part D, which is made air-tight by the leather collar b. The glass tube O is bent, that it may more conveniently be introduced under the receiver of a pneumatic apparatus. P, shews the manner of connecting the glass tube with the stop-cock.

